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VAPOR PRESSURES IN THE LIQUID SYSTEM $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$.
DERIVED THERMODYNAMIC DATA AND
A STRUCTURAL INTERPRETATION

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ADMINISTRATIVE INFORMATION

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ABSTRACT

By use of the transpiration method, the vapor pressures of the liquid system $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ between pure B_2O_3 and $\text{Rb}_2\text{O} \cdot \text{B}_2\text{O}_3$ have been measured. The vapor over the entire composition range was an equimolar mixture of Rb_2O and B_2O_3 . Data from other sources indicate that the vapor molecule should be RbBO_2 . The activity of the RbBO_2 in the melts showed a pronounced discontinuity at about 15 mole percent Rb_2O . The activity and other thermodynamic data were compatible with a liquid structure based on Biscoe and Warren's theory, which describes the structures of alkali borate glasses. The activity of the RbBO_2 in the melts and the vapor pressure of the RbBO_2 above the melts could be decreased by the addition to the melt of oxygen-complexing cations.

SUMMARY

The Problem

The work reported here is the first phase of a long term project devoted to studying chemical reactions occurring in liquid oxide systems. The approach is to measure vapor pressures over liquid oxides as a function of temperature and liquid composition. Thermodynamic data derived from these measurements are used as an aid in describing the reactions occurring in the liquids and the structure of the liquids themselves. The results obtained from these studies will contribute basic information to the expanding field of high temperature chemistry.

Findings

Vapor pressure equilibria over melts of the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ system have been studied in the temperature range of 875 to 1554°C. The vapor over all melts consisted of a complex molecule, RbBO_2 . Strong negative deviations from ideality were observed in the system. Thermodynamic data indicate that the liquid structure can be described by analogy with the corresponding crystalline or vitreous solids.

The liquid from pure B_2O_3 to a composition of about 17% Rb_2O -83% B_2O_3 consists of a more or less continuous network of trigonally and tetrahedrally coordinated boron-oxygen groups. At liquid composition between 17 and 28% Rb_2O some of the network bonds are broken but the network itself is not destroyed until the Rb_2O concentration exceeds 28%. From 28 to 50% Rb_2O the structure of the liquid changes to discrete, anionic rings.

The chemical activity of the RbBO_2 in the liquids, and its vapor pressure over the liquids, could be decreased by the addition of oxygen complexing cations.

VAPOR PRESSURES IN THE LIQUID SYSTEM $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$.
DERIVED THERMODYNAMIC DATA AND A STRUCTURAL INTERPRETATION.

INTRODUCTION

In recent years interest has increased in the chemistry of high temperature processes. Much work has been done on fused salt systems. Also important has been the study of fused oxide systems on which little has been done, however, except in slag and glass forming systems. Such comparative neglect undoubtedly is due primarily to the experimental difficulties inherent in working at the high temperatures required and in the extreme reactivity of most molten oxides.

As one phase of a program of high temperature research carried on at this Laboratory, it was decided to undertake a basic inquiry into the chemical reactions occurring in selected liquid oxide systems. A preliminary study of the interaction of rubidium vapor with solid oxides at high temperatures had shown that thermally stable compounds could be formed between rubidium oxide and certain acidic oxides.¹ Therefore rubidium oxide was used as one member of the system to be studied. Boron oxide was chosen as the other because it seemed likely to form comparatively stable compounds or complexes with rubidium oxide in the liquid state. The existence of complexes in solid alkali borate glasses has been postulated to explain their anomalous physical properties. It was felt that an investigation of the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ liquid system would contribute to an understanding of the structural relations in alkali-borate mixtures.

The experimental approach consisted of determining the chemical activity of the volatile component in the fused $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ mixtures by measuring its vapor pressure as a function of temperature and liquid composition. Deviations from ideality in the liquid mixtures could then be determined and an

explanation for these deviations made in terms of a structural model for the liquid. From the activity data, the free energy, heat, and entropy of mixing could be calculated and these values used to check the consistency of the structural model.

EXPERIMENTAL METHODS

The two most commonly used methods for high temperature vapor pressure determinations are the effusion method and the transpiration method. The effusion method requires that the sample be heated in a vacuum. Used with oxide systems, this might lead to undesirable decompositions, which could be avoided by heating the samples under ordinary atmospheric conditions. The transpiration method involves measuring the vapor pressure of the sample by slowly passing a measured amount of an inert carrier gas over the sample. Air can be used as the carrier gas, thus maintaining an oxidizing atmosphere over the sample. For this reason the transpiration method was chosen, and an apparatus was built which has been used to measure vapor pressures in air up to temperatures of about 1600°C (temperatures are given in °C throughout this report).

Description of Apparatus.

The apparatus consisted essentially of a furnace chamber into which a removable alumina tube containing the sample was inserted (Fig. 1). The furnace was heated inductively through power supplied by an Ajax 20-KW spark-gap converter. A cylindrical graphite crucible packed in powdered graphite insulation was used as a susceptor. The graphite susceptor was protected from oxidation by being lined on the interior with a dense, high purity alumina crucible and lid.

Two openings were provided into the furnace chamber. One was a fixed alumina tube on whose outer end were a window and an air inlet. The furnace temperature was determined by sighting a Leeds and Northrup optical pyrometer through the window; dry air was introduced through the inlet in order to keep the window clean and to maintain an oxidizing atmosphere in the furnace chamber. The second opening consisted of an open alumina tube through which a dense, gas-tight alumina sample tube could be inserted into the furnace chamber. The dense alumina parts were obtained from the McDanel Refractory Porcelain Co.

In that end of the sample tube which entered the furnace chamber was cemented a platinum capsule which contained the sample whose vapor pressure was to be measured. On the outer end of the sample tube was a window for optical pyrometer readings and an inlet where the carrier gas was introduced.

It was necessary that the sample capsule be made of platinum as rubidium vapor can form a thermally stable compound with alumina. The capsule consisted of a platinum cylinder about 1 cm in diameter and 3 1/2 cm long. One end of the cylinder was completely closed except for a hole about 1/2 mm in diameter which served as the inlet for the carrier gas. The other end of the cylinder was open. A close fitting platinum cap in the shape of a cylinder was made to fit over the open end of the capsule. The cap was provided with a 1/2-mm hole in its end for the outlet of the carrier gas.

The sample itself was fused onto a series of four adjacent loops bent in the end of a platinum wire. The platinum wire sample holder was secured in the capsule by passing the straight end of the wire through the hole in

back of the capsule for a distance of about 3 cm so that it rested against the interior top of the alumina sample tube. The loops of wire containing the sample were then balanced in the center of the capsule. The wire was not large enough to block the carrier gas entry hole completely. The platinum cap then could be placed over the end of the capsule and the whole assembly inserted into the furnace.

It was found that the sample, about 100 mg in weight, when melted, did not drop off the platinum wire loops. This arrangement was chosen because the rubidium content of the sample was to be determined by radioactive counting and it was planned to insert the whole sample into a crystal gamma counter. Also, a large area of the sample could be exposed, thereby making a saturated vapor pressure easier to maintain during the experimental runs.

During the runs, the temperature of the sample was determined by sighting an optical pyrometer through the window of the alumina sample tube onto the end of the platinum capsule. Previous measurements had shown that the temperature read off the back of the capsule was the same as that read by sighting through the gas inlet hole into the interior of the capsule, where black-body conditions prevailed. A correction for absorption in the window was applied. The optical pyrometer had been previously calibrated by the Leeds and Northrup company. By manual adjustments of the temperature control the temperature of the sample was kept constant to within about ± 1 to 2° .

During the runs, a measured amount of constantly flowing dry air had to be supplied through the alumina sample tube to act as the carrier gas. To accomplish this, two 1000-ml burettes were mounted in parallel so that

a measured volume of air could be forced from the burettes into the sample tube by the injection of a stream of silicone oil into the burettes. The oil was introduced into the burettes by siphoning from a Mariotte bottle, thus maintaining a steady flow during the run. The volume of air displaced was determined by reading the oil level in the burettes before and after each run. The air was dried by passage through anhydrous magnesium perchlorate before it was admitted to the burettes and also as it left. The temperature of the air in the burettes was determined by means of a mercury thermometer.

Preparation of Samples

The $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ samples were prepared by fusing radioactive Rb_2CO_3 and B_2O_3 together in a platinum dish. The Rb_2CO_3 was obtained from A. D. Mackay, Inc., and from K & K Laboratories, Inc. The Rb_2CO_3 was purified by dissolving in water, filtering, and recrystallizing by evaporation. The purity was then checked spectroscopically and negligible amounts of impurities were found.

Radioactive rubidium in tracer amounts was introduced into the carbonate by the use of radioactive Rb^{86}Cl supplied by Oak Ridge National Laboratory. The radioactive RbCl , in HCl solution, was evaporated to dryness in a platinum dish. The Rb_2CO_3 was dissolved in water and added to the radioactive RbCl in the platinum dish, and the solution was stirred well. The solution was then evaporated to dryness, and the radioactive Rb_2CO_3 was recovered and dried thoroughly. A negligible amount of chloride was introduced into the carbonate by this process.

The B_2O_3 was prepared by the dehydration of reagent grade boric acid obtained from J. T. Baker Chemical Co. The B_2O_3 was dried by heating in a platinum dish in air for several hours at 1000° . Weighed amounts of boron oxide and radioactive Rb_2CO_3 were fused together in a platinum dish and stirred well. The resulting $Rb_2O-B_2O_3$ mixture was left in the platinum dish and stored in a desiccator. Samples were removed by remelting the solution and dipping into the melt with a platinum wire. The liquid sample drops were quickly transferred to the loops on the platinum sample wire.

The initial vapor pressure determinations of pure B_2O_3 revealed irregularities in the data which were found to be due to insufficient dehydration of the B_2O_3 samples. In order to completely remove all interfering traces of water it was necessary to reheat the B_2O_3 samples on the platinum sample holder before weighing and inserting into the furnace chamber. This was done by mounting the platinum sample wires holding the B_2O_3 onto the end of an alumina rod and inserting the sample through a port into a furnace. The samples, approximately 100 mg. in weight, were dried for about two hours at 1000° . Because of the pronounced hygroscopicity of the carbonate and borates, all materials and samples were weighed in a dry box to avoid errors caused by the absorption of atmospheric moisture.

The alumina sample tube was also periodically baked at red heat with dry air being passed through it in order to remove all traces of moisture. These dehydration procedures were necessary as B_2O_3 can react with water vapor at high temperatures to form volatile hydroborates.² As the solutions became richer in Rb_2O the water was less tenaciously held and a less rigorous dehydration procedure was required. The mixture of 50% Rb_2O - 50% B_2O_3 dried easily at 600° for 1/2 hour. Samples of intermediate compositions were dried for about 1 hour at temperatures from $800-1000^\circ$.

Experimental Procedure

The transpiration method of measuring vapor pressures relies on a determination of the mass of sample vapor per unit volume of the carrier gas-sample vapor mixture. The sample vapor concentration is measured either by condensing and weighing the vaporized material that has been removed by a known volume of carrier gas or by observing the change in weight of the condensed phase of the sample before and after the passage of the known volume of carrier gas. The latter method was adopted here. To compute the vapor pressure of the sample it is necessary to know the molecular weight of its vapor species.

Considering the mixture of carrier gas and sample vapor, if the ideal gas law holds, then from Dalton's law of partial pressures,

$$P_S = \frac{N_S}{V} \cdot RT \quad (1)$$

where P_S = partial pressure of the sample vapor

V = total volume of carrier gas-sample vapor mixture

T = temperature at which V is measured

N_S = moles of sample vapor in V . Where the volume of the sample vapor is small compared with the volume of the carrier gas, the volume of the carrier gas may be substituted in Eq 1 as a close approximation for the volume of the carrier gas-sample vapor mixture. As the ratio of the carrier gas volume to the sample vapor volume varied from about 4000 to 100 during this experiment, the use of this approximation introduced a negligible error.

There are two sources of error inherent in the transpiration method. The first is that the carrier gas may be flowing over the sample too rapidly so that it leaves the sample capsule unsaturated with respect to the sample vapor.

The second is the loss by diffusion of the sample vapor independent of the loss via the carrier gas. By constructing the apparatus so that the orifices through which the carrier gas enters and leaves the sample capsule are small, and by using relatively high gas velocities, the loss due to diffusion could have been minimized. However, this was not possible in the apparatus described here. The platinum cup, which closed the end of the sample capsule, had to be fairly loose because at high temperatures it had a tendency to sinter to the platinum capsule and could not be removed without destroying the capsule. Also the gas velocity could not be ~~increased~~ so as to reduce the diffusion loss to a negligible value, without simultaneously undersaturating the carrier gas. These difficulties were eliminated as follows.

The removal of the sample vapor from the capsule may be considered to be the sum of two terms: the loss due to diffusion, which is time-dependent, and the loss due to the carrier gas, which is volume-dependent.

$$W = D \cdot \Delta t + S \cdot \Delta V \quad (2)$$

W = total weight loss of sample

D = rate of weight loss per unit time due to diffusion

S = weight of sample vapor in saturated carrier gas per unit volume

Δt = time interval of experimental run

ΔV = volume of carrier gas per run. This was essentially equal to the volume of carrier gas plus the volume of sample vapor.

Usually both the time of the run and the volume of the carrier gas can vary. However, if, for a series of runs at constant temperature, the time of run, Δt , is held constant while ΔV is varied, then the weight loss due to diffusion,

$D \cdot \Delta t$, is constant. Equation 2 becomes linear with two variables, W and ΔV . If the total weight loss, W , is plotted against ΔV , then the resulting plot should be linear with the intercept on the W axis equal to the diffusion loss and the slope equal to S or the saturation value of the sample vapor in the carrier gas. S may be determined directly in grams per liter and, after being converted to moles per liter, may be substituted directly in Eq. 1 for the term N_S/V .

This treatment assumes that D is independent of the rate of flow of the carrier gas. This is close to being true, since the greater part of the diffusion loss seems to occur both as the sample tube is entering the furnace and reaching temperature equilibrium before the flow of carrier gas is turned on and during the withdrawal and cooling process after the flow has ceased. During the runs the times of entry and of withdrawal and the time during which the carrier gas was flowing were held constant.

It is also assumed that S remains constant for the series of runs. This will be true as long as the carrier gas is saturated with the sample vapors. When the carrier gas velocity is too high and the gas is unsaturated, S will decrease as ΔV increases and the plot will no longer be linear. It was found that saturation was achieved for gas velocities up to about 25 ml/min.

In actual practice the plots were linear. The standard times of gas flow were either 40 or 80 min and the gas velocity varied from about 4 to 20 ml/min.

As a check on the experimental method, the vapor pressure of CsCl was measured at a series of temperatures between 800° and 900° . The vapor pressure vs. temperature curve was parallel with and about 7% greater than the curve derived from the vapor pressure data for CsCl tabulated by Kelley.³ The values

tabulated by Kelley were measured by a manometric method which indicated the total pressure over the liquid salt.⁴ This method gives a direct measurement of the pressure that is not dependent upon a knowledge of the molecular weight of the vapor.

Some uncertainty is associated with the CsCl vapor pressure values derived by the transpiration method because of the tendency of alkali halide vapor molecules to form dimers, thereby changing the molecular weights of the vapors. An estimate of this effect can be made by an extrapolation of the data of Datz, et al.,⁵ who determined the apparent molecular weights and degree of dimerization for a series of alkali halide vapors by measuring the pressure of known amounts of the salts in an enclosed volume. This calculation indicates that the mole fraction of dimer in the CsCl vapor varied from 0.20 to 0.28 over the temperature range of the transpiration runs. Recomputing the vapor pressure of the CsCl on this basis lowers the vapor pressure curve so that it falls about 15% lower than that of Kelley.

Margrave,⁶ in a discussion of the various methods for determining high temperature vapor pressures, has stated that different investigators frequently disagree by as much as 25 to 50% on vapor pressure measurements. Considering this possible region of error and that the values from Kelley were obtained by an entirely different experimental method than that used here, the agreement is considered to be good.

As a further check, the vapor pressure of pure B_2O_3 between the temperatures of 1440 and 1554° was measured and compared with the literature values. Again the agreement was quite good (See Fig. 2). These measurements are plotted and discussed in the next section of this report.

In the case of a two-component liquid where the vapor has a different composition than the liquid, the liquid composition will change during the run. In the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ solutions there was only one volatile constituent. During the runs, the samples became somewhat depleted in this constituent so that the actual vapor pressure decreased, giving an erroneously low weight loss. However, these data could easily be corrected. After the apparent vapor pressures of the volatile constituent were determined for a series of different compositions, a graph showing the change in vapor pressure as a function of composition was made. From this information and from a knowledge of the initial and final compositions of the samples, a curve could be constructed which corrected the observed weight losses for the effect due to the depletion of the volatile constituent. Theoretically, on the basis of the corrected vapor pressure values, a second curve of vapor pressure vs. composition should be constructed and the correction process repeated to get an even closer answer to the true vapor pressure. However, in practically all cases the second correction factor did not differ appreciably from the first. Usually this correction factor amounted to about 1 to 5% of the observed weight losses, except for the solution containing the least amount of Rb_2O , in which case some of the corrections were as much as 20 to 40%.

The total weight losses were determined by weighing the samples on the platinum wire loops in a dry box before and after the runs. The weight loss of the Rb_2O was determined by the loss in radioactivity during the run. Although gamma counting was used, there was appreciable self-absorption in the samples for which a correction was necessary. This difference in self-absorption manifested itself as a slightly different counting rate for samples of the same

weight and Rb_2O content but with different geometric shape or arrangement on the platinum wire loops. In order to eliminate any errors due to this effect, the apparent specific activity was computed for each sample prior to the run. This specific activity was defined as the gamma counting rate divided by the weight of the Rb_2O in the sample. The Rb_2O content was known from the total weight of the sample and from its initial percent composition of Rb_2O . During the run, the shape and arrangement of the sample on the wire loops did not change appreciably, so that there was no effect on the counting rate due to this geometrical factor. However, as the sample lost weight during the run, the magnitude of the self-absorption effect decreased and the specific activity at the conclusion of the run was greater than it should have been.

To correct for this, the specific activities of a series of samples of the same percent Rb_2O and the same shape but varying in total weight were determined. These results were plotted so that, the initial and final weights of a sample being known, its change in specific activity due only to its change in weight could be corrected for. These corrections usually amounted to about 1 to 2 % of the counting rates of the samples.

The B_2O_3 weight loss was measured by the difference between the total weight loss and the Rb_2O weight loss. As a check on these techniques, the compositions of some of the samples were determined after the runs by wet chemical analysis as well as by the radioactive tracer method. The determinations of the total weight of each component in the samples agreed to within 1 to 3 %, and experience indicated that the radioactive tracer method was as accurate as the chemical analysis method.

PRESENTATION OF DATA

Vapor pressure determinations were made over seven liquids varying in composition from pure B_2O_3 to 50 mole percent Rb_2O -50 mole percent B_2O_3 . The vapor pressure of B_2O_3 as a function of temperature is plotted in Fig. 2, where it is compared with data from other investigators. In computing the vapor pressure, the vapor species was assumed to be the monomer, B_2O_3 . This has been well established by direct evidence using mass spectrographic methods⁷ and an effusion-torsion technique.⁸

It can be seen from Fig. 2 that the vapor pressure data reported here agree very well with the extrapolated data of Speiser, Naiditch and Johnston.⁹ The vapor pressure data of both Speiser, et al. and Nesmeyanov and Firsova¹⁰ were obtained over a lower temperature range by use of the effusion method. The data of Soulen, Sthapitanonda and Margrave¹¹ were obtained by the transpiration method using dry, oxygen-free nitrogen as the carrier gas. The vapor pressures of Soulen, et al. are somewhat higher than those reported here.

These high values may have been caused by incomplete drying of the B_2O_3 samples. These authors report heating the samples up to 1000° for an hour or more. It has been shown here that, unless the samples are quite small, this procedure is insufficient to remove all interfering amounts of water.

The experimental data for the Rb_2O - B_2O_3 melts are presented in Table 1. Before vapor pressures can be calculated it is necessary to know the molecular weight of the vapor species. In the fourth column of Table 1 the experimentally observed compositions of the vapors are listed as mole percent Rb_2O . These figures are derived by use of Eq. 2. For each series of runs the weight losses of Rb_2O and of B_2O_3 were plotted against the volumes of carrier gas.

TABLE 1

Experimental Data

Comp. of Melt (mole %)	Sample Temp. (°C)	Corrected Sample Wgt. Loss (mg/L)	Mole % Rb_2O in Vapor
4.2% Rb_2O 95.8% B_2O_3	1201	1.4	66
	1235	2.6	41
	1267	5.2	46
	1302	8.6	40
	1343	17.6	39
		Avg.	<u>46</u>
11.1% Rb_2O 88.9% B_2O_3	1144	2.9	45
	1186	6.8	45
	1210	8.7	51
	1241	14.6	49
	1272	20.8	60
		Avg.	<u>50</u>
20.0% Rb_2O 80.0% B_2O_3	1026	3.3	51
	1062	7.6	58
	1083	10.8	55
	1108	12.5	47
	1139	23.3	57
		Avg.	<u>54</u>
28.0% Rb_2O 72.0% B_2O_3	956	5.9	63
	986	12.2	57
	1001	16.8	61
	1047	26.4	54
	1072	46.2	57
		Avg.	<u>58</u>
33.3% Rb_2O 66.7% B_2O_3	905	5.1	52
	941	10.6	51
	977	21.5	51
	997	29.6	53
	1021	43.5	50
		Avg.	<u>51</u>
50% Rb_2O 50% B_2O_3	875	6.2	50
	905	12.6	50
	930	20.5	50
	961	40.2	50
	992	67.6	50
		Avg.	<u>50</u>

The ratio of the slopes of the Rb_2O plots to those of B_2O_3 gave the weight ratio of the Rb_2O to B_2O_3 in the vapor; these figures were then converted to mole percent Rb_2O .

The most interesting aspect of these data is that the average vapor composition is close to 50% Rb_2O throughout the whole range of liquid compositions. This strongly suggests that the vapor is composed of a compound of equi-molar parts of Rb_2O and B_2O_3 . Compound formation in the vapor is further indicated by the fact that, at these temperatures, there should be no measurable vapor pressure due to free B_2O_3 from the solutions, and that the apparent vapor concentration of B_2O_3 increases throughout the series of liquids as its concentration in the liquids decreases.

An extra series of experimental runs for each liquid was made using dry argon instead of air as the carrier gas. This was done to determine if the sample vapors decompose, and produce free oxygen. This would occur if Rb_2O and B_2O_3 vaporized independently, as Brewer, et al.,^{12,13} have shown that the alkali oxides, with the exception of Li_2O , will vaporize predominantly by decomposition to the elements. The sample weight losses were the same when argon (99.975% pure) was used as a carrier gas as when air was used. This indicates that the presence or absence of oxygen did not influence the vaporization equilibrium and that the sample vapors did not decompose.

As the transpiration method can give no more indication of the vapor species, further information must be obtained from other sources. The most direct evidence concerning the nature of this vapor species comes from mass spectrographic studies of the vapors from lithium and sodium metaborates reported by Buchler and Berkowitz-Mattuck.¹⁴

These authors report that the vapor in equilibrium with sodium metaborate between 620 and 830°C consisted predominantly of monomeric sodium metaborate, NaBO_2 . Appreciable amounts of the dimer were observed, as well as minor amounts of several other molecules. The proposed structure of the monomeric molecule is a linear $(\text{O-B-O})^-$ group with the sodium ion attached at an angle at one end. This structure also has been reported by Akishin and Spiridonov in an electron diffraction study of lithium and sodium metaborate vapors at 1200 to 1500°C¹⁵

Additional evidence of the stability of the monomer is furnished by the infrared spectral studies of Morgan and Staats.¹⁶ These authors, after studying traces of metaborate dissolved in solid solutions of alkali halides, concluded that the metaborate ion occurs in these dilute solutions as the monomer with a linear structure.

The monomer HBO_2 has been reported as the major species in the vapor of metaboric acid by White, *et al.*¹⁷ The gaseous molecule also consists of a linear O-B-O group with the hydrogen attached at an angle at one end.

Buchler and Berkowitz-Mattuck also reported data on the infrared spectra of gaseous NaBO_2 and CsBO_2 . Both of these vapors gave similar spectra with absorption peaks at 5.2 and 17 μ . As a check on the molecular species of vaporized rubidium metaborate, the infrared absorption spectrum of the vapor over the 50% Rb_2O melt was obtained. This was accomplished by heating the melt in a platinum crucible inside an alundum tube furnace closed at each

end with NaCl windows. Directed through one end of the tube furnace was a globar source and at the other end was a Perkin-Elmer infrared spectrometer, Model 12. The furnace was operated at 1000 to 1200°. The background radiation from the furnace was eliminated by use of a rotary beam-chopping wheel between the globar source and the furnace window. This device modified the incoming light signal to 13 cycles/sec so that, with a modification in the analyzer unit of the spectrometer, the direct radiation from the furnace itself could be electronically filtered out.

The spectrum of the rubidium metaborate showed a prominent absorption peak at 5.1 μ . The peak at 17 μ was not sought, as it lay beyond the limits of the spectrometer. This result indicates that the vapor over rubidium metaborate is similar to that over sodium and cesium metaborates, and that it consists mainly of the monomer RbBO_2 .

An attempt to measure infrared spectra of vapors over other $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ melts with lower concentrations of Rb_2O was not successful due to the much lower vapor pressures. Unfortunately, the infrared apparatus was not available for modifications for use at higher temperatures. However, as the vapor concentration over all the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ melts of varying compositions was, within experimental error, close to 50% Rb_2O -50% B_2O_3 , it was felt that the same molecular species was present in all cases and that this species was RbBO_2 .

Due to the small weight losses, occurring during the runs, the experimental error in determining the $\text{Rb}_2\text{O}/\text{B}_2\text{O}_3$ ratio could be fairly large. This is apparent in the most dilute solution, 4.20% Rb_2O , where the total weight losses amounted to only 1 to 10 mg. From Table 1 it can be seen that the

experimentally measured mole percent of Rb_2O in the vapor over this melt varies considerably from one series to another although the average comes out close to 50 %. On the other hand, in the case of the 50.0 % Rb_2O melt, where it was possible to evaporate much larger amounts without changing the composition of the liquid, the measured Rb_2O concentration in the vapor was equal to 50 % for each series of runs.

Of the six melts, the only important deviation from a vapor composition of 50 % Rb_2O was in the case of the 28.0 % Rb_2O melt. In this case the average vapor concentration was 58 % Rb_2O . Whether this represents a significant difference in the vapor composition or whether it is due to experimental variation is not known. In view of the lack of precision in determining the vapor composition, and because this variation occurs in only one melt out of six, it will be assumed here that the vapor composition over the 28.0 % Rb_2O melt is the same as that over the other melts. However, it should be emphasized that mass spectrographic studies of vapors over other oxide and fused salt systems have shown a surprising variety of vapor molecules over single melts. It is likely that there are other vapor species present over the Rb_2O - B_2O_3 melts, and that the ratios of these species may change with variations in liquid composition and temperature. However, lacking more precise information, it is felt that the assignment of RbBO_2 as the major vapor species over all the melts is the best possible choice.

On this basis the vapor pressures of RbBO_2 for each series of runs was computed by converting the corrected sample weight losses, column 3 of Table I, to moles per liter and substituting these quantities for the term n_g/V in Eq. 1. The term T in Eq. 1 refers to the temperature of the carrier gas at which its volume was measured and was in the range 24 to 26°.

The values for the computed vapor pressures have been plotted in a log P vs 1/T graph (Fig. 3) and the lines drawn according to the least-squares fits. The vapor pressure for each melt can also be expressed by the equation

$$\log P = A - \frac{B \times 10^3}{T (^{\circ}\text{K})}$$

The constants A and B and the temperature interval over which the vapor pressure of each melt was measured are listed in Table 2.

The heat of vaporization of RbBO_2 from pure liquid rubidium metaborate (50 % Rb_2O) has been computed from the slope of the log P vs 1/T graph and is found to be 58.7 ± 1.7 Kcal/mole (90 % confidence limit) over the temperature range of the experimental measurements.

RESULTS AND DISCUSSION

By means of the vapor pressure data and by assuming ideal behavior of the RbBO_2 at low partial pressures, the activity of the RbBO_2 in the melts may be obtained by use of the formula $a = P/P^0$, where P is the partial pressure of the RbBO_2 over the melt and P^0 is the RbBO_2 pressure over pure liquid rubidium metaborate. The activities of the RbBO_2 at 1050° over each melt have been calculated and plotted as a function of liquid composition (Fig. 4).

This graph shows that the activity of the RbBO_2 is essentially zero until a composition of approximately 15 % Rb_2O is reached. Near this point the activity begins to increase appreciably and, after a composition of about 28 % Rb_2O is reached, the activity increases linearly with increasing Rb_2O content. This behavior suggests the formation of complex structural groups in the melts.

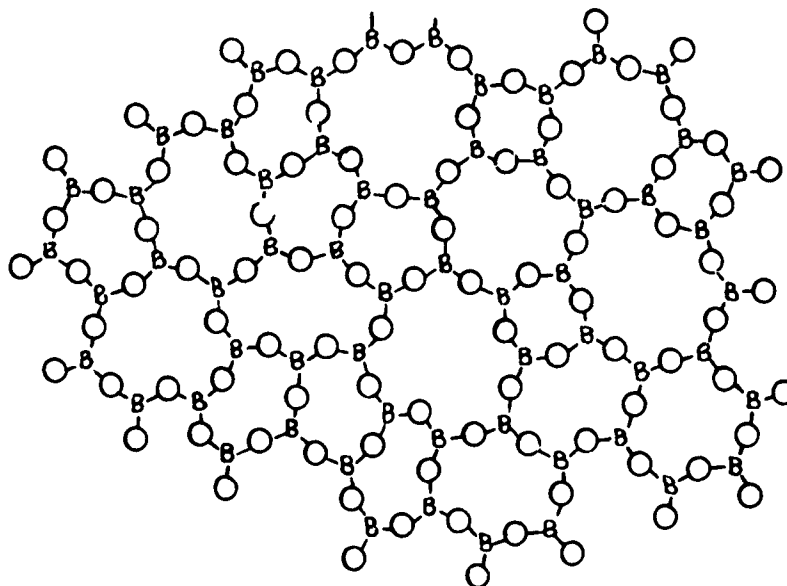
TABLE 2

Constants for Vapor Pressure Equation for RbBO_2

$$\log P = A - \frac{B \times 10^4}{T (^{\circ}\text{K})}$$

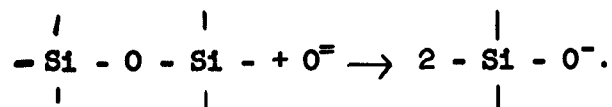
Liquid comp., mole % Rb_2O	A	B	Temp. range, $^{\circ}\text{C}$
4.2	9.275	1.895	1201-1343
11.1	6.969	1.445	1144-1272
20.0	6.821	1.296	1026-1139
28.0	6.696	1.178	956-1072
33.3	7.335	1.218	905-1021
50.0	8.256	1.283	875- 992

Similar abrupt changes in several of the physical properties of alkali metal borates at about this same composition have given rise to the term "boric oxide anomaly". These properties include density, viscosity, expansivity, heat of solution and infrared spectra. A structural explanation of the boric oxide anomaly was first suggested by Biscoe and Warren.¹⁸ In conformance with Zachariasen's network theory of glasses, Biscoe and Warren pictured boron oxide glass as consisting of a three-dimensional random network of boron and oxygen ions in which each boron ion is surrounded by three oxygen ions lying in a plane and each oxygen ion is situated between two boron ions.



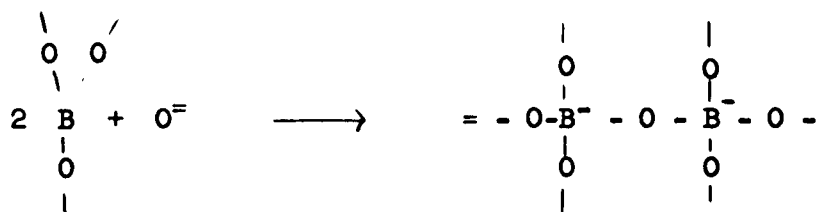
This structure is quite similar to that of silica glass, which is also pictured as a continuous three-dimensional network consisting of silica ions surrounded by four oxygen ions in a tetrahedral arrangement, with each oxygen ion situated between two silicon ions. As alkali oxide is added to a silica glass, the silicon retains its tetrahedral coordination with respect to oxygen, so that the only way in which the added oxygen can be accommodated in the

structure is by it being inserted into a silicon-oxygen bond thereby causing a rupture of the bond and the formation of two non-bridging oxygen groups:



The alkali metal ions fit into holes in the network near the non-bridging oxygens. In this manner the continuous silica network is progressively broken down as alkali oxide is added.

The analogous process in the case of the boron oxide glasses is modified by the ability of the boron to vary its coordination number with respect to oxygen. Biscoe and Warren postulated that as alkali oxide is added to the trigonally coordinated boron-oxygen network, the additional oxygen enters into the structure, not by breaking a bond of adjacent trigonal BO_3 groups and forming a pair of non-bridging oxygen groups but by coordinating tetrahedrally with and forming a bridge between two trigonal BO_3 groups:



This forms a structure intermediate between the tetrahedral network of vitreous silica and the trigonal network of vitreous boron oxide.

This process does not continue indefinitely but comes to a halt when the composition reaches about 16 mole % alkali oxide. The extra oxygens furnished by the addition of further alkali oxide do not form a continuous tetrahedral network with the boron but rupture the boron-oxygen bonds, forming non-bridging boron-oxygen groups analogous to the case of the silicon-oxygen network

previously described. It is the beginning of this transition from a strong, continuous network to a broken, open structure which causes the abrupt changes in physical properties referred to as the boric oxide anomaly.

The theory of Biscoe and Warren concerning the changes in coordination number of boron was based on X-ray diffraction studies of glasses. Although this method has been shown to be imprecise enough to cast doubt on the conclusions of Biscoe and Warren,¹⁹ later work using nuclear magnetic resonance has verified the change in coordination of boron from three to four as alkali oxide is added. However, there is no general agreement concerning the amount of boron which becomes tetrahedrally coordinated and at what composition the process ceases.^{20,21} Although Biscoe and Warren's theory has been criticized and alternative theories proposed, none of these theories have been as useful in explaining the properties of alkali borate glasses. Zachariasen's network theory and Biscoe and Warren's extension have been generally accepted as valid for, at least, an approximate picture of the structure of vitreous boron oxide and the alkali borate glasses.

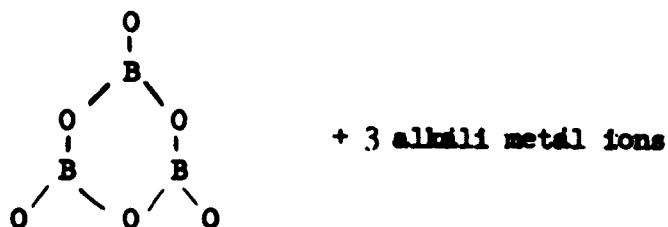
Bearing the foregoing interpretation of the boric oxide anomaly in mind, one can now return to the data on the activity of the RbBO_2 in the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ melts (Fig. 4) where the activity-composition curve showed a pronounced break at about 15 % Rb_2O . The similarity of this change to the physical changes referred to above in connection with the boric oxide anomaly leads one to surmise a structural arrangement in the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ melts analogous to that in the alkali borate glasses. Further, from the activity composition curve, the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ melts can be considered as two liquid systems. The first system extends from pure B_2O_3 to a liquid of an approximate composition of 15 %

Rb_2O -85 % B_2O_3 , and the second from 15 % Rb_2O -85 % B_2O_3 to 50 % Rb_2O -50 % B_2O_3 (rubidium metaborate). For a detailed model of the Rb_2O - B_2O_3 system molecular structures must be postulated for each of these three liquids and probable interactions predicted among them as they are mixed.

Proposed Model for the Rb_2O - B_2O_3 Liquid System.

Assuming from the evidence discussed above that the structure of the melts is similar to that of the corresponding solid, the structure of the pure liquid B_2O_3 will be a more or less continuous but irregular network of boron atoms trigonally coordinated by oxygens. Mackenzie²² experimentally verified this structure for liquid B_2O_3 and pointed out that the structure was temperature-dependent. He suggested that, as the temperature increases the continuous network progressively breaks by the formation of terminal - B = O groups.

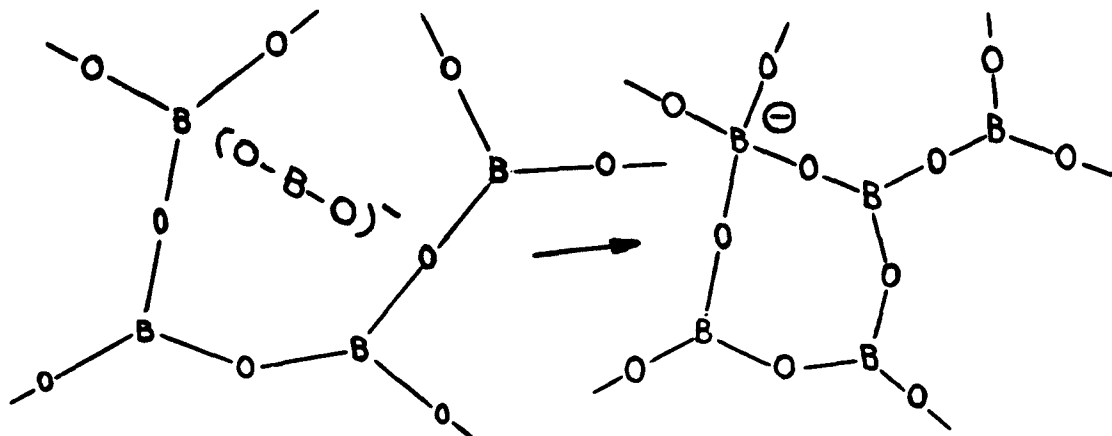
In considering the structure of liquid rubidium metaborate, the structures of crystalline sodium and potassium metaborates consist of complex, six-membered, anionic rings.²³ The rings contain 3 borons and 3 oxygens, and the borons are trigonally coordinated with the oxygens as shown below. The sodium and potassium ions fit into holes in the rigid structures formed by the large anions.



These six-membered rings apparently are quite stable as there is evidence that they occur in the vapors of metaboric acid and some boron oxy-halides.²⁴ It shall be assumed here that liquid rubidium metaborate also consists of these rings. However, it is also possible that the liquid metaborate consists of chains or various combinations of rings and chains.

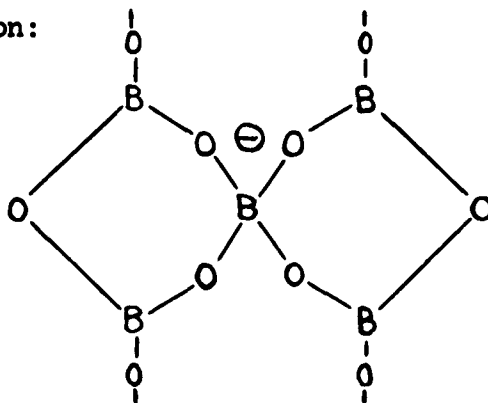
It has been stated earlier that the rubidium metaborate vapor consists of the monomer, RbBO_2 , and that the same monomer exists when the metaborate, in trace amounts, forms solid solutions in alkali halide crystals. However, it seems highly unlikely that the monomer exists in the pure liquid metaborate due to the strong tendency of BO_2^- ions to polymerize, forming the stable trigonally coordinated groups. Further evidence of a high degree of association in the liquid is the large entropy of vaporization. The values were calculated for both B_2O_3 and RbBO_2 at temperatures where the partial pressures of each vapor was 10^{-3} atm: for B_2O_3 , a highly associated liquid, 44.6 cal/deg. mole; for RbBO_2 , 51.5 cal/deg. mole.

Assuming, then, that the liquid boron oxide consists of a more or less continuous network of trigonally coordinated borons with oxygens and that the metaborate liquid consists of discrete six-membered anionic rings, what structural rearrangement can be pictured as the two liquids are mixed? If Biscoe and Warren's theory is followed, as the metaborate is added to the boron oxide, tetrahedrally coordinated boron groups should be formed until a liquid composition of about 16 % Rb_2O -84 % B_2O_3 is reached. It is a reasonable assumption that the six-membered metaborate rings break up into smaller groups (probably $[\text{O} - \text{B} - \text{O}]^-$ ions) in the solution and that these groups enter the boron oxide network by the formation of tetrahedrally coordinated BO_4 groups as shown:



This process is postulated to continue until a liquid composition of about 16.7 % Rb_2O -83.3 % B_2O_3 is reached, at which point about 1/5 of the borons in the liquid are tetrahedrally coordinated.

Abe has suggested a possible structural unit for glasses of this composition.²⁵ This unit is based on two six-membered rings joined by a tetrahedrally coordinated boron:

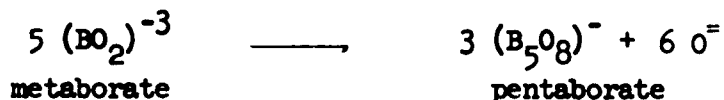


These units are attached at the corners and form a continuous network in which each tetrahedral group is separated by two trigonal groups.

This same structural unit has been reported as an isolated ion in potassium pentaborate tetrahydrate²⁶ and as a continuous structural element in crystalline potassium and rubidium pentaborates.²⁷ By X-ray diffraction and infrared studies, Krogh-Moe has found structural similarities between crystalline and vitreous potassium pentaborate.²⁸ He concludes that structural elements of the crystalline phases exist in the glass in unknown proportions.

Although Abe did not believe that this pentaborate structural unit exists in alkali borate mixtures at temperatures higher than their melting points, it will be postulated here that this unit persists in the melts and that the structure of a melt of composition 16.7 % Rb_2O -83.3 % B_2O_3 may be pictured as approaching a more or less continuous network based on this structural unit.

Further, in conformance with Biscoe and Warren's ideas, when liquid metaborate is added to liquid pentaborate, the formation of tetrahedrally coordinated boron groups ceases and, instead, the continuous network begins to be broken down with the formation of non-bridging boron-oxygen groups. This process can be visualized if it is realized that, from a formal point of view, the net effect of adding the metaborate is to furnish oxygen ions to the liquid pentaborate. After solution, the boron-oxygen groups of the metaborate become indistinguishable from the boron-oxygen groups of the pentaborate, except for the excess oxygen ions:



The excess oxygens are then inserted into the network structure by breaking a B - O - B bond and forming two non-bridging oxygen groups, B - O⁻, for each added oxygen ion.

As further metaborate is added, the network is progressively destroyed, the tetrahedral groups are broken down and the liquid approaches the discrete, six-membered anionic ring structure of pure liquid metaborate.

Compatibility of the Liquid Model With Experimental Data

It is possible to check certain properties deduced from the proposed liquid model with some experimentally measured properties of the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ melts. Consider first the activity of the RbBO_2 in the melts. Normally the activity of a component of a liquid is proportional to its mole fraction. In the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ melts, the RbBO_2 does not exist as a discrete entity and its concentration has to be defined in terms other than that of the RbBO_2 molecule.

The structure of the RbBO_2 molecule, containing the $(\text{O}-\text{B}-\text{O})^-$ group, suggests that it could vaporize much more readily from a condensed phase that contains non-bridging $\text{B} - \text{O}^-$ groups than one that contains only a continuous network of non-bridging $\text{B} - \text{O} - \text{B}$ groups. On this basis, let the "mole fraction" of the RbBO_2 in the melt be defined as the fraction of boron atoms which are attached to non-bridging oxygens.

By means of this definition it is seen that, regardless of whether the structure of liquid metaborate is assumed to be discrete anionic rings or chains, the mole fraction of the RbBO_2 in the pure metaborate melt will be unity. Further it is seen that the mole fraction of the RbBO_2 is zero for liquid compositions between pure B_2O_3 and 16.7 % Rb_2O . This follows from the model postulating that no non-bridging oxygen groups are formed until the Rb_2O content is in excess of 16.7 %.

As the Rb_2O content of the melts increases beyond the pentaborate composition, non-bridging oxygen groups begin to form and the mole fraction assumes a finite value. The actual value will depend upon what bonds in the liquid are broken first. If a degree of stability is granted to the pentaborate

group, it seems reasonable to suppose that the first $\text{B} - \text{O} - \text{B}$ bonds to be broken will be those which join the pentaborate units together. Also it is reasonable to suppose that the entering anion will prefer a site which is as far away as possible from the negatively charged central tetrahedral group. The composition of the liquid at which, on the average, one of the four bonds from each pentaborate group will be broken will be 28.6 % Rb_2O -71.4 % B_2O_3 . At this composition one out of five boron atoms will be attached to a non-bridging oxygen, and the mole fraction of the RbBO_2 will be 0.20. It should be noted that at this point three-quarters of the bonds joining the pentaborate groups are still unbroken and the continuous network structure is essentially intact. It is not until further bonds are broken that the network begins to disintegrate appreciably. It is known that in solidified alkali borate melts the glassy structure persists until a composition of about 33 % alkali oxide is reached. At higher alkali oxide concentrations it is difficult to prevent crystallization.

In considering which bond is likely to be broken next, it might be assumed that the remaining three bonds joining the pentaborate groups would be broken before the bonds of the central tetrahedral group. However, this would mean that at the composition 50 % Rb_2O -50 % B_2O_3 the pentaborate groups would exist as a discrete anion. This group does not exist in the solid metaborate structure and it is unlikely that it exists in the liquid.

If it is assumed that after the breaking of the first bond joining adjacent pentaborate groups it is equally likely that any of the remaining bonds will be broken, the mole fraction of RbBO_2 can be calculated for mixtures up to the metaborate composition.

Assuming an activity coefficient of unity, the activity of the RbBO_2 will be equal to its mole fraction in the melts. The theoretical activity calculated on this basis is very close to the experimentally determined activity over the entire composition range of the melts, as shown in Fig. 4.

As a further check on the proposed model, the free energy, enthalpy and entropy of mixing of liquid B_2O_3 and RbBO_2 as a function of liquid composition were computed. The relative partial molar free energy of RbBO_2 in the melts was computed from the experimental activities by use of the expression:

$$\Delta \bar{F}_{\text{RbBO}_2} = RT \ln a_{\text{RbBO}_2}$$

The relative partial molar enthalpy, $\Delta \bar{H}_{\text{RbBO}_2}$, of the RbBO_2 was determined by the difference in slope of the $\log P$ vs $1/T$ graphs of pure RbBO_2 and of RbBO_2 in the various melts. The relative partial molar entropy of the RbBO_2 was computed using the relationship:

$$\Delta \bar{F}_{\text{RbBO}_2} = \Delta \bar{H}_{\text{RbBO}_2} - T \Delta \bar{S}_{\text{RbBO}_2}$$

From the partial quantities, the integral free energy, enthalpy and entropy were obtained by a graphical integration of the equation,

$$\Delta G = N_{\text{B}_2\text{O}_3} \int_{\substack{N_{\text{RbBO}_2} \\ N_{\text{B}_2\text{O}_3}}}^{\substack{N_{\text{RbBO}_2} \\ N_{\text{B}_2\text{O}_3}}} \Delta \bar{G}_{\text{RbBO}_2} d \left[\frac{N_{\text{RbBO}_2}}{N_{\text{B}_2\text{O}_3}} \right],$$

$N_{\text{RbBO}_2} = 0$

where G refers to either free energy, enthalpy or entropy.

The corresponding relative partial molar quantities for B_2O_3 were found by use of the equation

$$\Delta G = N_{B_2O_3} \Delta \bar{G}_{B_2O_3} + N_{RbBO_2} \Delta \bar{G}_{RbBO_2}$$

These thermodynamic quantities are measured relative to pure liquid B_2O_3 and $RbBO_2$ as the standard states and they represent average values over the temperature range of the experimental data. These quantities are plotted in Figs. 5, 6 and 7.

The curve of integral heat of mixing shows a negative maximum of about -5.0 Kcal/mole at a composition of 14 to 15 % Rb_2O and decreases to small positive values at a composition range of about 40 to 50 % Rb_2O . The heat of mixing of two ideal liquids is zero throughout the whole composition range. In general, where two dissimilar liquids are mixed so that there is a heat effect but no compound formation in the liquid, the heat of mixing curve should rise to a maximum near the mid-point and should decline more or less symmetrically on either side. The pronounced asymmetry in the curve in the B_2O_3 - Rb_2O system suggests compound formation in the liquid. The decline in this curve after a composition of about 14 to 15 % Rb_2O indicates a stable molecular structure at about the pentaborate composition (16.7 % Rb_2O).

The large decrease in the heat of mixing at compositions rich in $RbBO_2$ can be interpreted as a tendency toward immiscibility. This can be shown more clearly if the Rb_2O - B_2O_3 system is divided into two liquid systems, B_2O_3 - RbB_5O_8 (pentaborate) and RbB_5O_8 - $RbBO_2$. The heat of mixing of B_2O_3 and $RbBO_2$ to form the pentaborate can be subtracted from the integral heat of mixing values, and the heats of mixing of the two new systems can then be computed relative to pure liquid B_2O_3 , $RbBO_2$ and RbB_5O_8 . These results are shown in Fig. 8.

The system B_2O_3 - RbB_5O_8 , consisting of mixtures of two structurally similar network liquids, behaves normally in that the heat-of-mixing curve is negative, with no gross asymmetries throughout the entire composition range. The RbB_5O_8 - $RbBO_2$ system, however, shows strong positive heats of mixing. This indication of immiscibility is caused by the mixing of two structurally dissimilar liquids, the network liquid, rubidium pentaborate, and the ionic liquid, rubidium metaborate. The fact that the liquids are miscible is due to the large increase in entropy of mixing in this composition range (Fig. 7).

Returning to Fig. 6, it is seen that the relative partial molar heats of mixing of B_2O_3 and $RbBO_2$ reach a maximum and a minimum respectively at about 28 % Rb_2O . If it is recalled that the partial molar quantities are partial differentials of the corresponding integral quantities with respect to changing composition, the maximum-minimum at the composition 28 % Rb_2O represents the point at which the heat content of the solution is changing most rapidly with changes in composition. From the proposed model, it is seen that at this composition (28.6 % Rb_2O) one of the four inter-pentaborate bonds have been broken and a transition zone occurs where there is a rapid change from a closely associated network liquid on the one hand to a liquid composed of discrete anions on the other. As has been pointed out before, this corresponds physically to the limit near which glass structures can be formed from the melt. At higher Rb_2O contents, the melts tend to crystallize upon solidification.

Shartsis and Capps have reported data on the heat of mixing of solid alkali oxides and boron oxide to form alkali borate glasses.²⁹ Their heat-of-mixing curves covered the composition range from pure B_2O_3 up to about 33 % alkali oxide. The curves were smooth and showed no maxima or points of inflection.

However, the basic reaction in this process studied by Shartsis and Capps is between free oxygen ions furnished by the alkali oxide and the boron-oxygen network of the B_2O_3 glass. This is quite different from the basic reaction reported here which is the reaction between an oxygen already attached to a boron atom, $\text{B} - \text{O}^-$ and the boron oxygen network. An extrapolation of Shartsis and Capps' data indicate the heat of formation of one mole of crystalline KBO_2 from K_2O and B_2O_3 is about -40 KCal. This large heat of formation of the $\text{B} - \text{O}^-$ group masks the boric oxide anomaly by obscuring the smaller effect due to the pentaborate formation in the mixture. The boric oxide anomaly is observed, however, in the heats of solution of alkali borate glasses in nitric acid as reported by Shartsis and Capps. These curves show a minimum at about 20 % alkali oxide. The boric oxide anomaly is not masked in this case as the heats of solution do not include the energy required to completely remove an oxygen ion from the boron groups.

Looking now at the entropy of mixing curves for the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ systems (Fig. 7), it can be seen that the integral entropy curve exhibits small negative values in the B_2O_3 rich region and increases to large positive values beyond the pentaborate composition. Also shown is the excess entropy of mixing curve. The excess entropy represents the difference between the actual entropy of mixing of the system and what the entropy would be if the system behaved ideally; i.e., it is a measure of the departure from ideality of the system. (It should be noted that the excess heat of mixing is equal to the actual heat of mixing of any system because the ideal heat of mixing is zero.)

It is seen from Figs. 6 and 7 that the excess entropy of mixing is generally negative in the regions where the heat of mixing has the largest negative values. This is due to the formation of the stable and comparatively ordered structure of the pentaborate network from the relative disordered B_2O_3 network and the anionic rubidium metaborateliquids. In the Rb_2O -rich regions where the pentaborate structure does not form and the liquid mixture consists of disordered network fragments and anionic groups, the heat of mixing decreases and the entropy increases to large positive values. The partial molar entropy curves for B_2O_3 and $RbBO_2$ show a minimum and maximum at 28% Rb_2O and their interpretation is similar to that of the partial molar enthalpy curves.

Variation of $RbBO_2$ Activity by Complex Formation

A feature of the proposed model for liquid alkali borates is the concept of measuring the activity of the $RbBO_2$ in terms of the mole fraction of non-bridging boron-oxygen groups. It follows that any process which decreases the activity of the $\text{B} - O^-$ groups in the melt also lowers the vapor pressure of the $RbBO_2$. This might be done by adding a third cation to the melt, which would form a strong complex with the non-bridging oxygen ions. This would not only reduce the concentration of non-bridging oxygen groups but also, depending upon the oxygen complexing ability of the added cation, tend to reconstitute the liquid network.

This concept was tested experimentally. A series of radioactive rubidium metaborate melts were prepared, each with a third oxide whose cation was likely to form a stable complex with oxygen ions in the melt. The cationic composition of each melt was 45 mole percent B^{+3} , 45 mole percent Rb^{+} and 10 mole percent

added third cation. The vapor pressure over each melt was measured at 925° and the results compared with the vapor pressure of pure rubidium metaborate at the same temperature. Any decrease in the vapor pressure of the RbBO_2 beyond that due only to dilution should be due to the complexing of the $\text{B} - \text{O}^-$ group in the melt and the corresponding decrease of the activity of the RbBO_2 .

The extent of the decrease of the vapor pressure which might be due only to dilution of the rubidium metaborate by the third oxide is difficult to compute because of the lack of knowledge of the kind and concentration of the ions or ionic groups in the melt. A rough estimate of this decrease might be made by assuming that the melt contains a ratio of 45 moles of Rb-B cationic groups to 10 moles of added cation or 82 mole percent Rb-B groups. This would cause a decrease in the vapor pressure of about 18 % if it were due to dilution alone. It is interesting to note that the decrease of the vapor pressure of the RbBO_2 by the addition of B_2O_3 corresponding to this concentration amounts to about 19 %.

The vapor pressure of the RbBO_2 over the melts was computed on the basis that the only vapor species was RbBO_2 . This assumes that the added oxides did not vaporize from the melts either independently or in combination with the rubidium oxide. All of the added oxides are relatively non-volatile at 925° except MoO_3 which apparently formed a very stable complex in the melt and did not vaporize. The assumption that the vapor species was RbBO_2 was checked by computing the ratio of Rb_2O weight loss, as determined by radioactive assay, to the total weight loss. This ratio was the same as that associated with the vapor over pure rubidium metaborate, except where SiO_2 and ZnO were added to the melts. In these cases the concentration of Rb_2O

in the vapor apparently decreased somewhat. In view of these experimental uncertainties, the results of this section should be regarded as only an approximate guide to the behavior of the complexing oxides in the rubidium metaborate melts.

It was found empirically that a plot of the percent decrease of the RbBO_2 pressure against an artificial factor computed by multiplying the ionization potential (in Kcal/mole) times the radius squared (in angstrom units) gave a roughly linear relationship.

This procedure can be justified qualitatively by the fact that the anionic complexing power of the added cation should be proportional to its electric field strength and to its surface area. That is, the stronger the electric field of the cation, the greater will be its attraction for oxygen ions; and the larger its surface area, the more easily it can accommodate a greater number of oxygen ions with less geometrical strain. The ionization potential of the cation was taken as a measure of its anionic attracting power and its radius squared was taken as a relative measure of its surface area. These results are plotted in Fig. 9. From the graph it can be seen that Mo^{+6} , Nb^{+5} , V^{+5} and, to a lesser degree, Ti^{+4} were quite effective in complexing the non-bridging oxygens and decreasing the RbBO_2 vapor pressure. The other ions had little more effect than the boron itself.

It was also noted that several of the added oxides, apparently by virtue of their complexing powers, reconstituted the liquid network so that some of the melts solidified to a glass or mixture of glass and micro-crystals. This was determined by observing crushed samples of the solidified melts under a polarizing microscope. In general, those ions which caused the

greatest decrease in vapor pressure also tended to convert the crystalline metaborate to a glass. These results are noted in Fig. 9.

Other Views on Coordination Changes of Boron

The liquid model discussed in this report has been based largely on Biscoe and Warren's and Abe's structural theories. These concepts have been criticized in a series of papers by Krogh-Moe and others, wherein the general concern is with determining the relative concentrations of trigonally and tetrahedrally coordinated borons. In an early paper, Grjotheim and Krogh-Moe,¹⁹ using the structure of crystalline boron oxide as a model, suggested that boron oxide glass contains a significant amount of tetrahedral BO_4 groups and that, as alkali oxide is added, the coordination of the boron changes from four to three.

However, later work by Silver and Bray²⁰ and by Krogh-Moe, et al.,²¹ using nuclear magnetic resonance techniques, have demonstrated that the boron in boron oxide is indeed trigonally coordinated and does change to a tetrahedral configuration as alkali oxide is added. There is, however, an apparent discrepancy between Silver and Bray's and Krogh-Moe's results and Biscoe and Warren's theory. According to Biscoe and Warren and Abe the formation of tetrahedral groups ceases at about 16.7 % alkali oxide, at which point the mole fraction of tetrahedrally coordinated boron is 0.20. Silver and Bray's results on soda borate glasses indicate that the number of tetrahedrally coordinated borons increases until a concentration of about 20 % Na_2O has been reached, at which point the mole fraction of tetrahedral boron is 0.40. Beyond this point the rate of increase of tetrahedral boron decreases. However,

those authors point out that their method makes the experimental values of the mole fraction of tetrahedral boron too large as the concentration of Na_2O increases. In view of the experimental uncertainty, the authors do not feel that their results are in contradiction to Biscoe and Warren's theory.

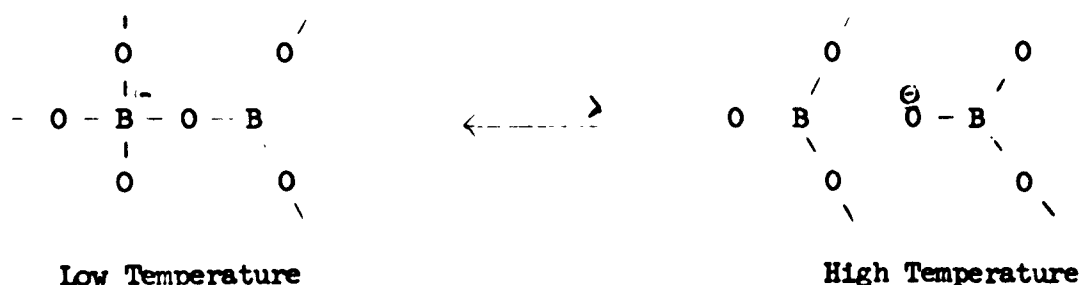
Krogh-Moe, et al. have studied a series of potassium borate glasses also using the nuclear magnetic resonance method. Their results are consistent with the rule that each mole of alkali oxide added to boron oxide converts two boron atoms from trigonal to tetrahedral coordination. Their data indicates that this process is continuous up to at least a composition of about 30 % K_2O - 70 % B_2O_3 at which point about 43 % of the borons are tetrahedrally coordinated. These results contradict Biscoe and Warren's theory. Furthermore, Krogh-Moe has questioned the notion that the formation of tetrahedral groups beyond a composition of 16.7 % alkali oxide creates an unstable situation by pointing out that tetrahedrally coordinated boron exists in greater concentrations in the polyanions of many crystalline borates.

Krogh-Moe has suggested an alternative theory for the structure of alkali borates. The main features of this theory are, first, tetrahedrally coordinated boron forms until at least a composition of 33 % alkali oxide has been reached and 50 % of the borons are in a tetrahedral configuration; and second, a mechanically induced coordination change of boron exists, such that the application of pressure favors the formation of tetrahedral groups.^{30,31} By means of this approach, Krogh-Moe has been able to explain some of the unusual physical properties of vitreous boron oxide and alkali borate glasses.

However, the results of the RbBO_2 vapor pressure measurements reported here do not agree with Krogh-Moe's theory. The fact that the activity and

derived thermodynamic data for this system show pronounced changes at about 15-17 % and at 28 % Rb_2O is consistent with the general theory of Biscoe and Warren and of Abe. In order to conform with the ideas of Krogh-Moe, the thermodynamic data should be continuous until a composition of at least 33 % Rb_2O is reached.

The two theories may be reconcilable if it is assumed that an equilibrium exists between trigonal and tetrahedral boron groups which is not only affected by the addition of alkali oxide but is also temperature-dependent so that increasing the temperature decreases the concentration of tetrahedral groups. Shartsis originally suggested this explanation of the anomalous viscosity data of the alkali borates.³² If it is assumed that the tetrahedral groups are relatively more stable at low temperatures, their existence can be understood in high concentrations in cool glasses and crystals containing up to 33 % alkali oxide. As the temperature increases, the equilibrium shifts to favor the formation of trigonal groups with non-bridging oxygen.



This thermal shift in equilibrium is pronounced only at alkali oxide concentrations greater than about 16.7 %. Apparently the tetrahedrally coordinated boron group in the pentaborate structure forms a stable configuration which can persist at high temperatures. Tetrahedral groups formed in excess of this composition are more unstable and more sensitive to temperature changes.

Evidence From Physical Properties of Alkali Borates Relating to the Temperature Effect on Boron Coordination

If this process occurs, then certain physical properties of the glasses and melts should show an anomalous temperature-dependence. As has been mentioned, Shartsis, et al, have used this concept to explain the variation in viscosity of the alkali borates. It has been generally believed that the conversion of planar, trigonally coordinated boron groups to three-dimensional, tetrahedral groups by the addition of alkali oxide should increase the viscosity of the mixture. This behavior is closely followed by alkali borates at low temperatures. The data of Shartsis, et al., show that at 500° after a small initial decrease at about 2 % alkali oxide, the viscosity of the mixture increases with increasing alkali oxide content. However, at higher temperatures, the initial decrease becomes more pronounced. At 800 and 900° the viscosity decreases until about 10 % alkali oxide has been added. The viscosity then increases slightly until about 20-22 % alkali oxide after which it begins to decrease markedly. This behavior is explainable if it is assumed that the equilibrium between trigonal and tetrahedral borons is affected by temperature as well as by alkali oxide concentration. At low temperatures, as small amounts of alkali oxide are added, the tetrahedral configuration is favored and the viscosity increases. As the temperature is increased, a small number of the tetrahedral groups revert to trigonal groups with non-bridging oxygens and the viscosity decreases. However, as more alkali oxide is added at the higher temperatures, the equilibrium shifts again in favor of the tetrahedral groups and the viscosity increases somewhat and reaches a maximum near 20 % alkali oxide. After this point,

tetrahedral groups are no longer formed at high temperatures. Instead, the network bonds are broken as alkali oxide is added with a consequent decrease in viscosity.

The initial decrease in viscosity at low alkali oxide concentrations is probably caused by a very small percentage of the tetrahedral groups changing to trigonal groups. The magnitude of this change is indicated by the addition of equal amounts of alkali oxide. As Mackenzie³³ has pointed out, the addition of about 2.5 % alkali oxide reduces the viscosity of silica at 1700° by a factor of about 10⁴. The same amount of alkali oxide reduces the viscosity of boron oxide at 600° by only a factor of 1.5 and at 1000° by a factor of 6. In the case of silica, the addition of alkali oxide results only in the formation of non-bridging oxygen groups. On the other hand, in the case of boron oxide, the predominant effect of the addition of alkali oxide is to create tetrahedral groups with only a small percentage of non-bridging groups formed. The relative viscosity changes of silica and boron oxide indicate that the fraction of tetrahedral groups reverting to trigonal groups and non-bridging oxygens must be very small.

Similar temperature variations occur in the case of the density and expansivity of alkali borates.³⁴ At 800-1000°, the density increases as alkali oxide is added. At about 12 to 15 % alkali oxide the rate of increase begins to decrease and a maximum density is reached at about 30 to 35 % alkali oxide. The density is dependent upon the added alkali oxide and the structure of the liquid; as the network structure of the liquid is maintained at these temperatures until about 28 % alkali oxide, the added alkali oxide fits into the structure, causing a net increase in density up to

this point. Beyond this point, the network breaks down rapidly and the relaxation of the structure results in a net decrease of density as alkali oxide is added. On the other hand, as alkali oxide is added at 25°, the density increases more or less linearly up to the limits measured (about 32 % Na₂O and 39 % K₂O). This again is explicable if it is assumed that at low temperatures tetrahedral groups continue to be formed with no discontinuities until at least 33 % alkali oxide.

The expansivities of the alkali borates at 800 to 1000° also show a pronounced change at 17 to 22 % alkali oxide. Below this range the expansivities increase only slightly as alkali oxide is added, which agrees with the proposed formation of a stable pentaborate network. Above this point, adding alkali oxide causes the network to breakdown and the expansivities to increase sharply. On the other hand, the expansivities at 25° are practically constant upon 32-40 % alkali oxide being added. This again indicates that, at low temperatures, there is no discontinuity in the structure as alkali oxide is added up to these limits.

If an equilibrium does exist in the alkali borate mixtures between tetragonal groups and trigonal groups with non-bridging oxygens, then it should be possible to affect this equilibrium chemically as well as thermally. If a cation with a strong affinity for oxygen is added to the melt, it will form complexes with the non-bridging oxygens. This effectively decreases the activity of the non-bridging oxygen groups and diminishes their tendency to form tetragonal groups as the melt cools. In this fashion the concentration of tetrahedral borons in the cool glass could be effectively decreased.

Furthermore, the extent of complexing and the extent of the decrease of tetrahedral borons should be proportional to the complexing power of the added

cation. The relative complexing powers of a series of cations has already been qualitatively measured by the procedure described in the previous section of this report in which the change in activity of RbBO_2 was measured by its change in vapor pressure upon the addition of the third oxides.

There is also the possibility of using nuclear magnetic resonance techniques to study the differences in tetrahedral coordination in glasses at room temperature and melts at high temperature if the melts are quickly chilled. However, this process may not be effective in freezing in the high-temperature structure as the transition from tetrahedral coordination to trigonal coordination involves very little atomic rearranging so that it might proceed at an appreciable rate at relatively low temperatures.

An indication of the temperature range at which this transition may occur is furnished by the work of Smith and Rindone.³⁵ These authors report data on the high temperature heat contents and entropies of four crystalline alkali borates and the glasses of the same composition. From their data the entropies of transition from the crystalline to the vitreous state can be computed; the results are plotted as a function of temperature in Fig. 10. It can be seen that for each of the mixtures studied the entropy of vitrification markedly increases in the temperature range 300 to 500°.

By assuming that the crystal structure is not appreciably affected by increasing temperature, it is possible to interpret these entropy changes as reflecting a pronounced change in the glass structure as the glass is heated past a critical temperature. At lower temperatures the equilibrium favors the tetrahedrally coordinated borons and the structure of the glass is similar to that of the crystal as postulated by Krogh-Moe. At temperatures

higher than the critical point the equilibrium favors the formation of trigonally coordinated boron and non-bridging oxygens so that the structure of the glass changes relative to that of the crystal and approaches that of the liquid borates. This transition is marked by the pronounced increase in entropy of vitrification.

Unfortunately, no entropy data are available for the crystal-glass transition for mixtures containing 17 % or less alkali oxide. In these cases the structure is postulated to be thermally stable and there should be no pronounced changes in the entropy-temperature graph.

Infrared studies of alkali borate glasses have been made by Anderson, Bohon and Kimpton,³⁶ by Jellyman and Procter,³⁷ by Moore and McMillan,³⁸ and by Krogh-Moe.³⁹ The results of the first three sets of authors are in disagreement with the nuclear magnetic resonance studies and with the interpretations of Krogh-Moe. All of these authors are in substantial agreement with the structures proposed by Biscoe and Warren and Abe. Krogh-Moe has criticized the basic interpretations of the infrared measurements of these authors. His results lead him to believe that the limitations of the infrared method when applied to extended network lattices are such that no reliable information regarding the coordination change of boron can be obtained by infrared spectrometry.

SUMMARY

The results of vapor pressure measurements in the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ system indicate that the vapor species is an equi-molar compound of Rb_2O and B_2O_3 . Evidence from other sources suggests that the molecular species is RbBO_2 . The

activity of the RbBO_2 in the melts shows an abrupt change at about 15 % Rb_2O . Changes in other physical properties of alkali borates at about this composition have given rise to the expression "boric oxide anomaly".

A model for the structures of the liquids in this system has been described which is based on the theories of Biscoe and Warren and of Abe concerning the structures of alkali borate glasses. Liquid B_2O_3 is pictured as an irregular, three-dimensional network composed of rings and chains of trigonally coordinated boron-oxygen groups. As Rb_2O is added to the liquid, the network is preserved since the added oxygen ions form bridging tetrahedral groups with the borons until a composition of about 17 % Rb_2O is reached. At this point 20 % of the borons are tetrahedrally coordinated and the liquid structure approximates the structure of crystalline rubidium pentaborate. As further Rb_2O is added, the oxygen ions break the continuous network by the formation of non-bridging boron-oxygen groups. The network structure persists until a composition of about 28 % Rb_2O is reached. As Rb_2O is added beyond this composition the network rapidly disintegrates and the liquid structure approaches that of rubidium metaborate which is envisaged as consisting of discrete, six-membered anionic rings of trigonally coordinated boron-oxygen groups.

The activity of the RbBO_2 was equal to its mole fraction in the melts when the mole fraction was defined as the fraction of boron atoms attached to non-bridging oxygens. The activity of the RbBO_2 could be decreased by the addition of cations which form complexes with the non-bridging oxygens. This results in a decrease of the RbBO_2 vapor pressure and, in some cases, a reconstitution of the liquid network.

On the basis of the work of other investigators it was pointed out that the equilibrium between tetrahedrally and trigonally coordinated borons, which leads to the change of physical properties of the boron oxide anomaly, is probably temperature-dependent and that the anomalous results should disappear at low temperatures. Further, it can be predicted that this equilibrium could be influenced by the addition to the mixture of oxygen complexing cations.

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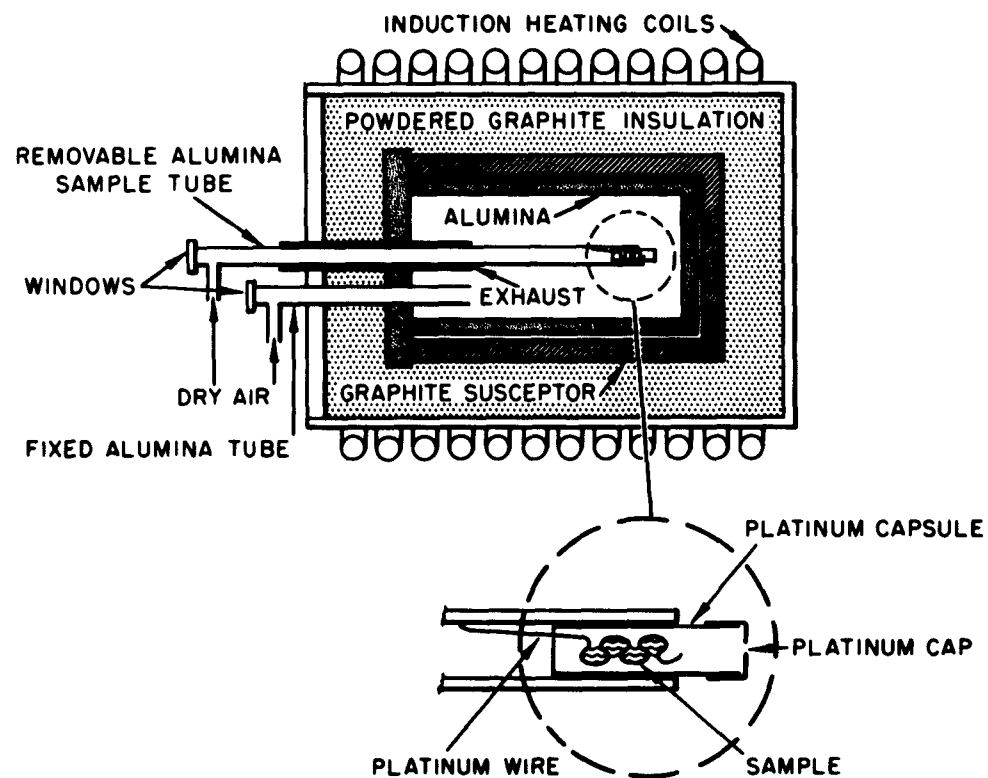


Fig. 1 Schematic drawing of high temperature vapor pressure apparatus

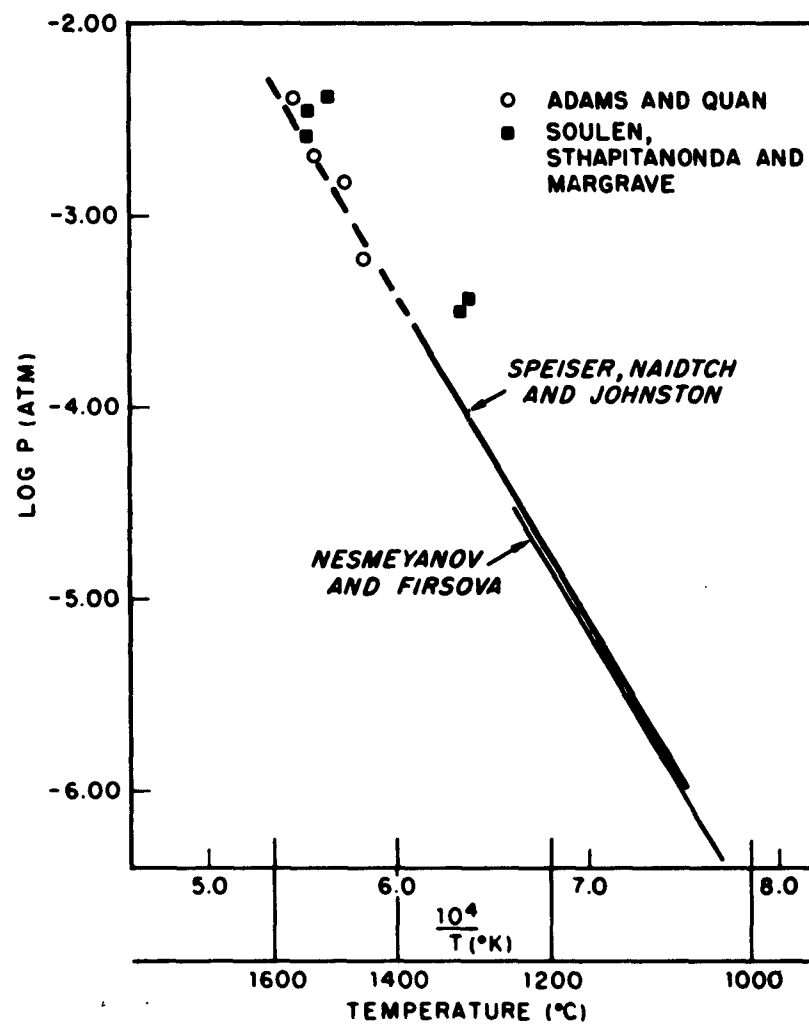


Fig. 2 Vapor pressure of B_2O_3

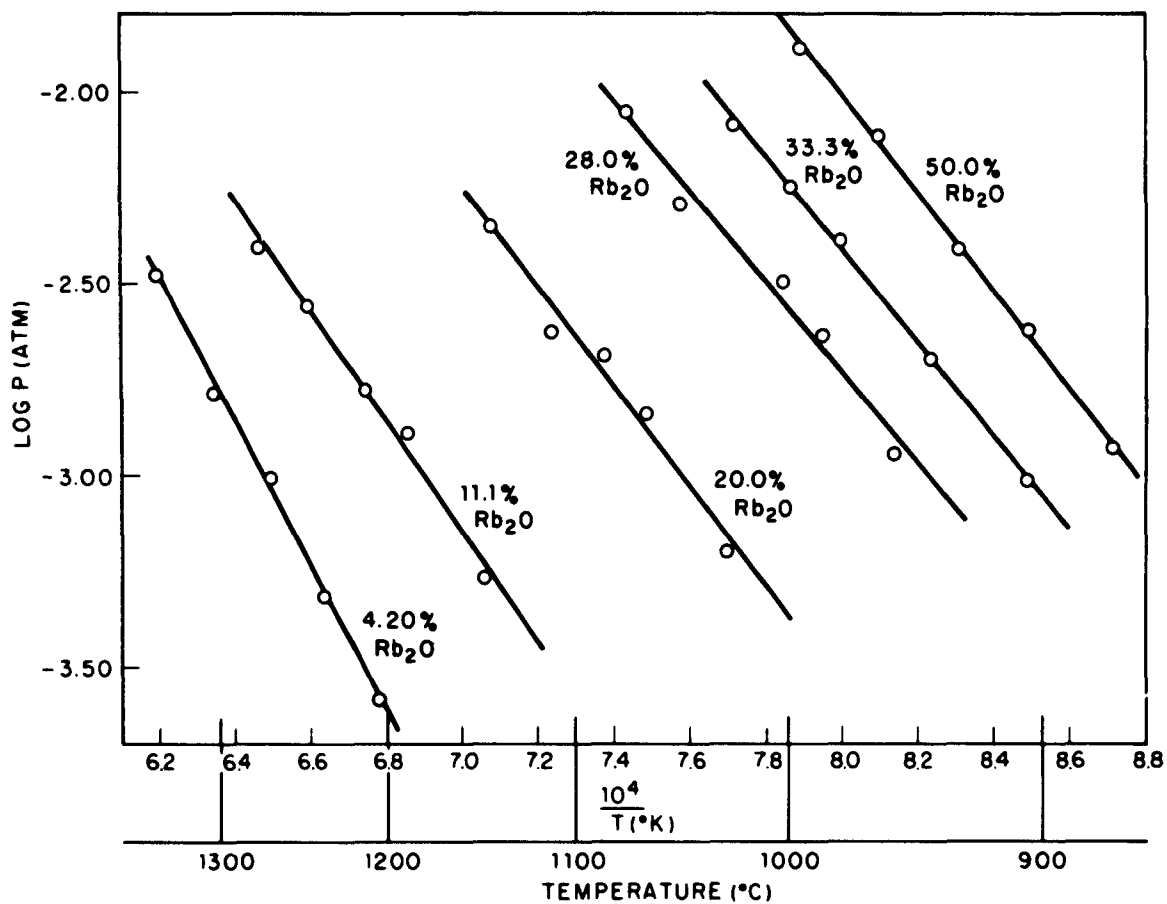


Fig. 3 Vapor pressure of RbBO_2 over $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ melts

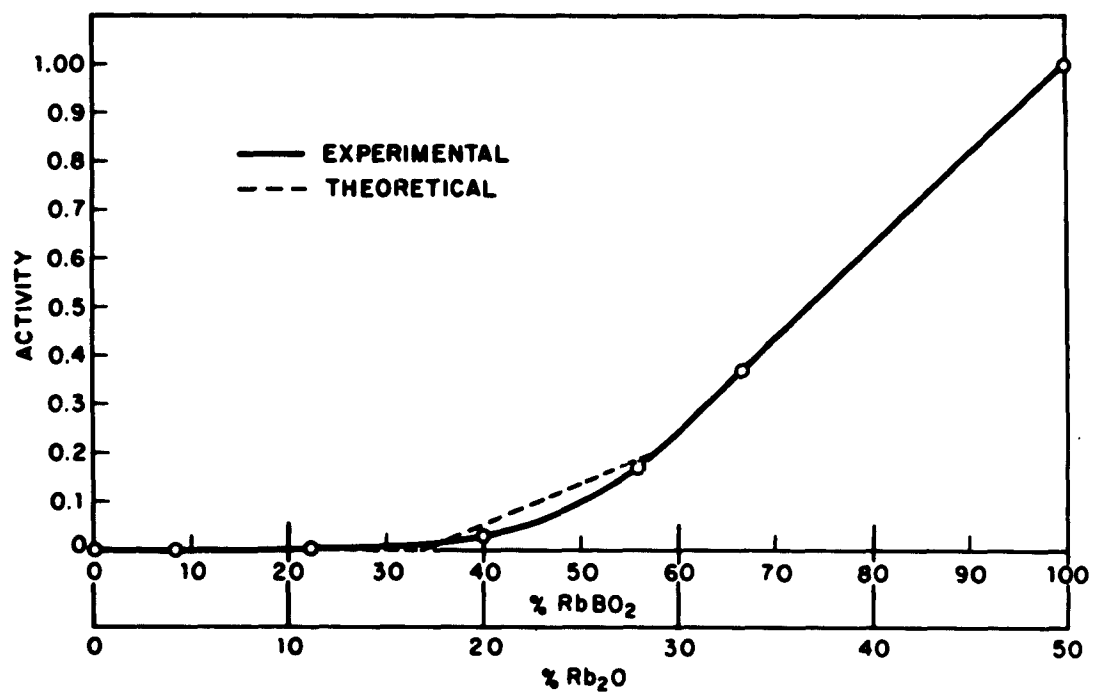


Fig. 4 Activity of RbBO_2 in $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ melts at 1050°

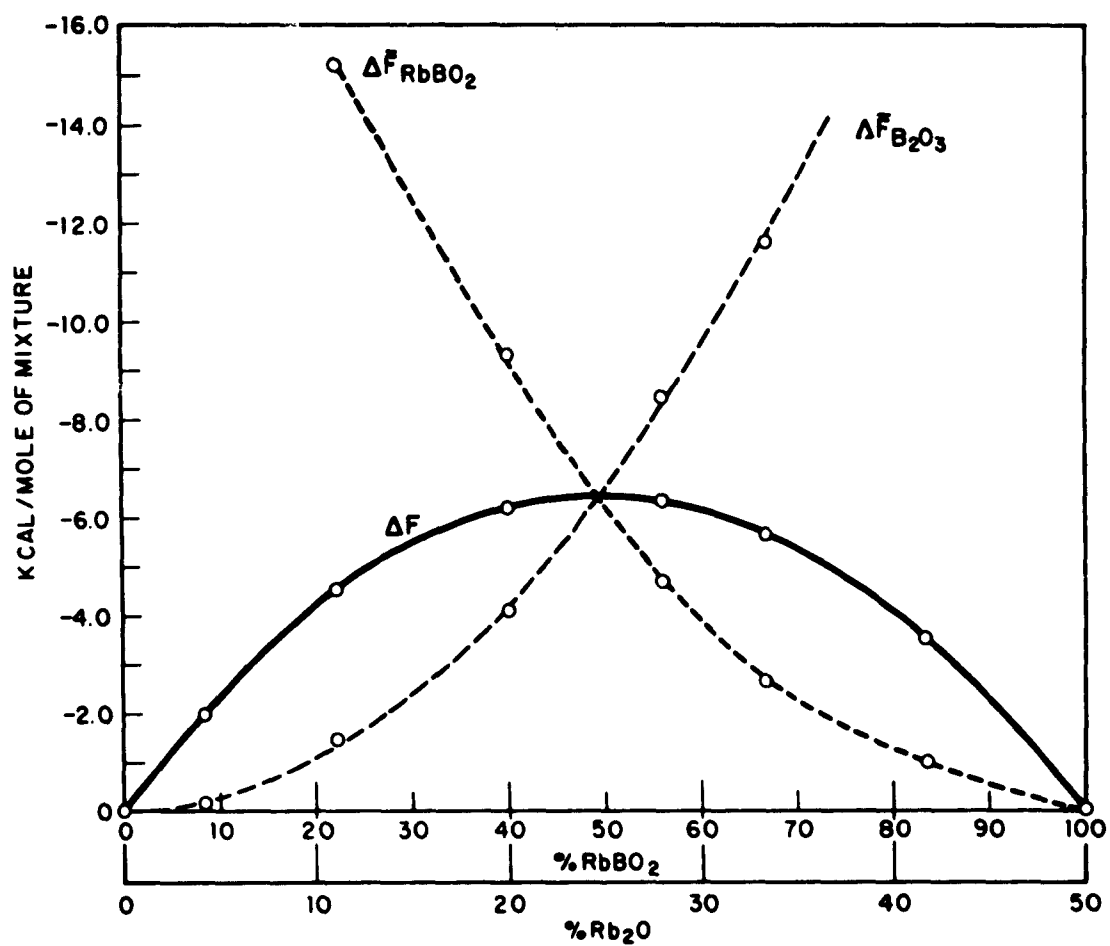


Fig. 5 Relative partial and integral free energies of mixing liquid B₂O₃ and RbBO₂ to form one mole of mixture at 1050°

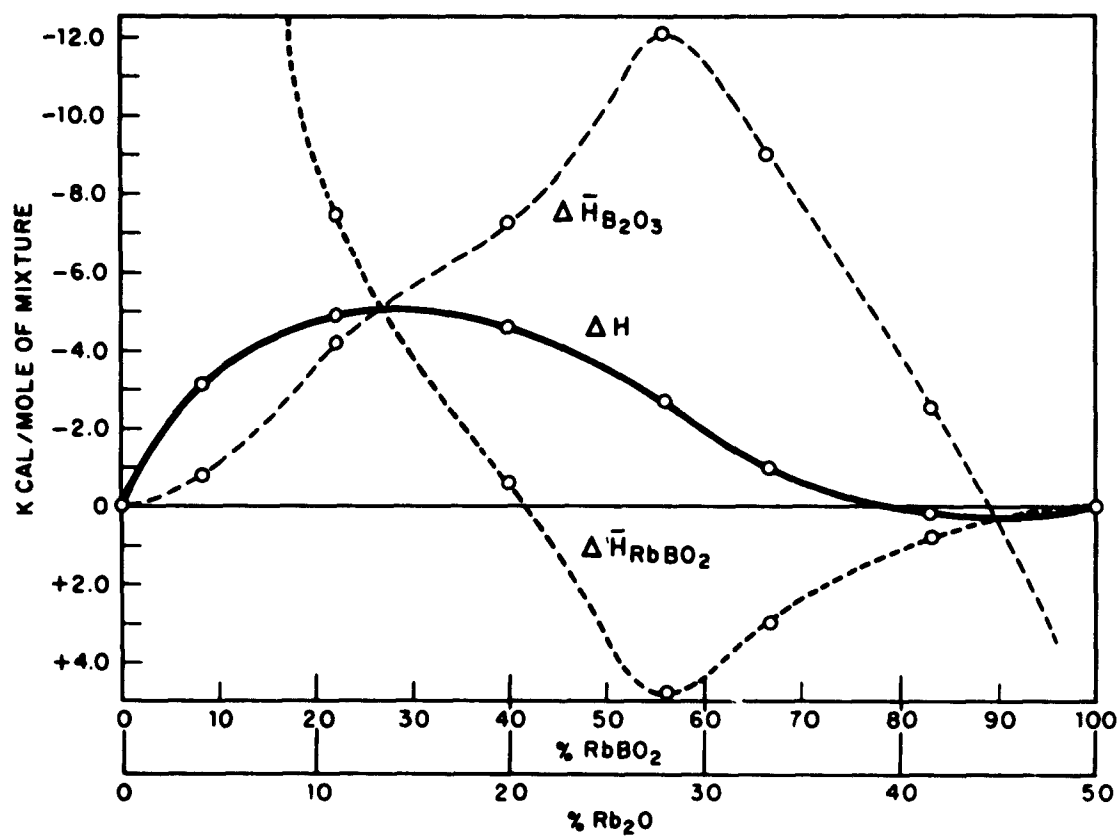


Fig. 6 Relative partial and integral heats of mixing

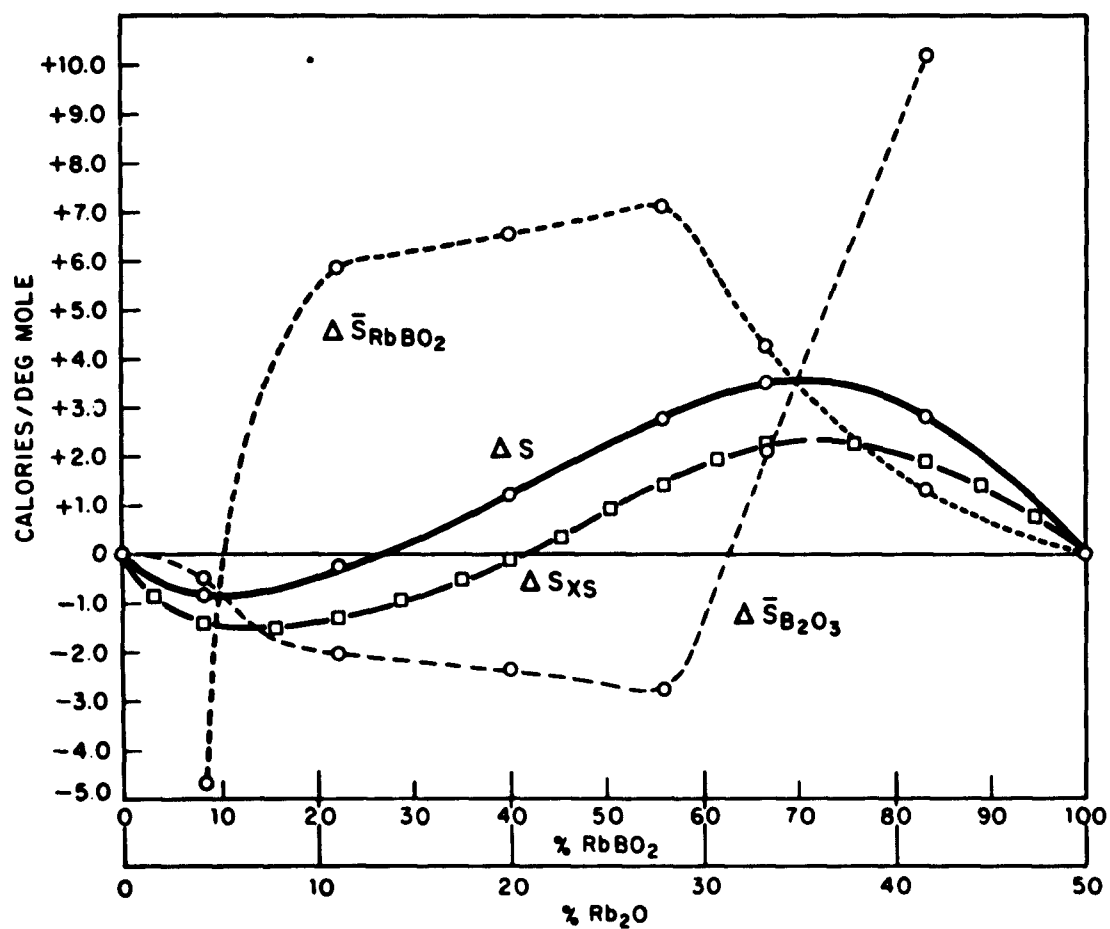


Fig. 7 Relative partial and integral entropies of mixing and excess entropy of mixing

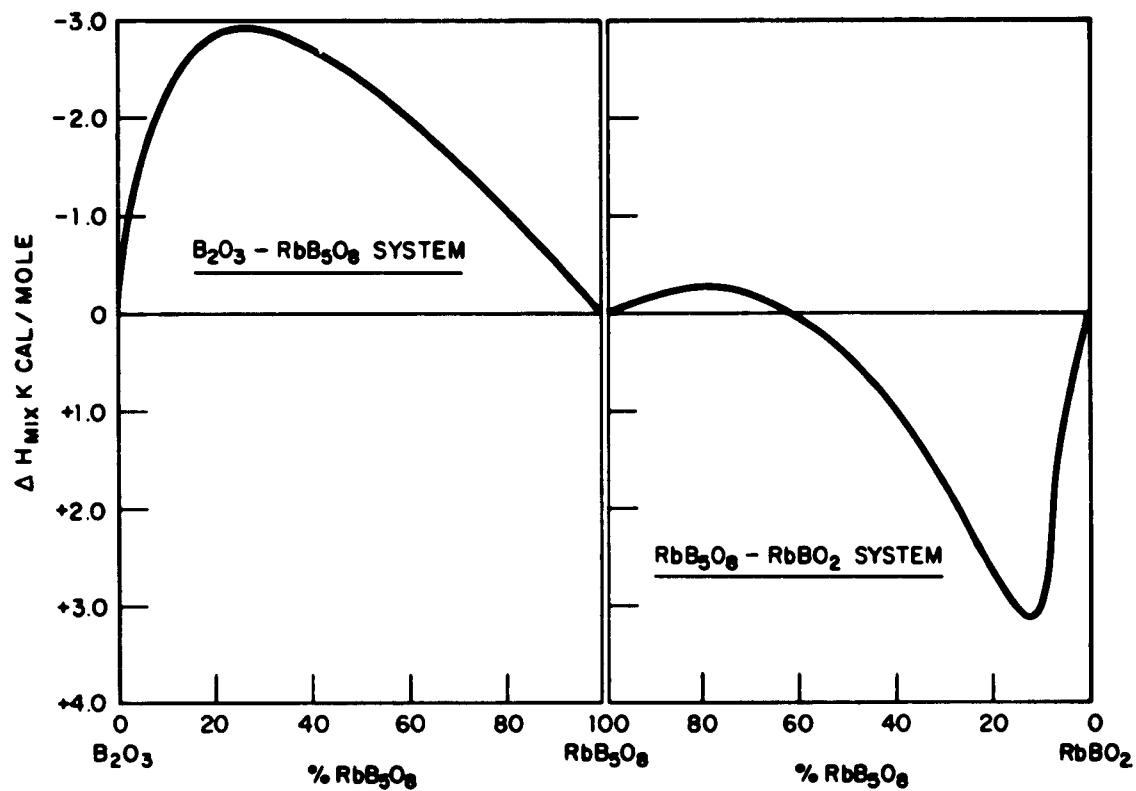


Fig. 8 Heat of mixing

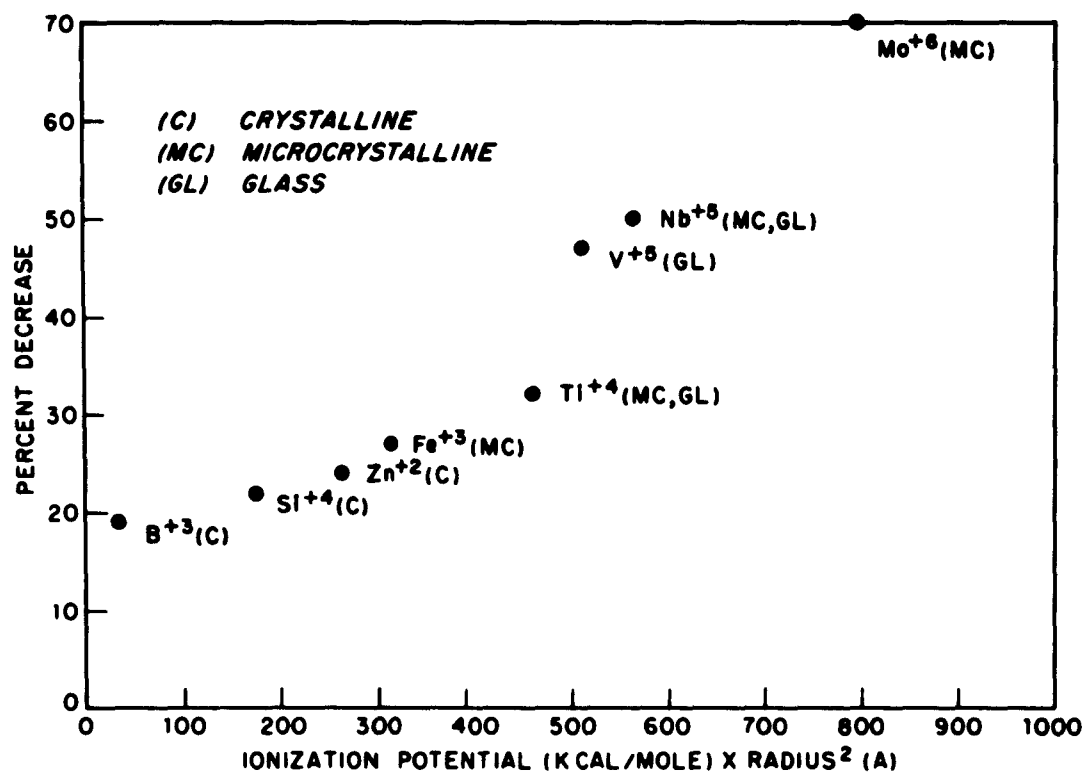


Fig. 9 Percent decrease of RbBO₂ vapor pressure upon the addition of complexing cations. $T = 925^{\circ}$

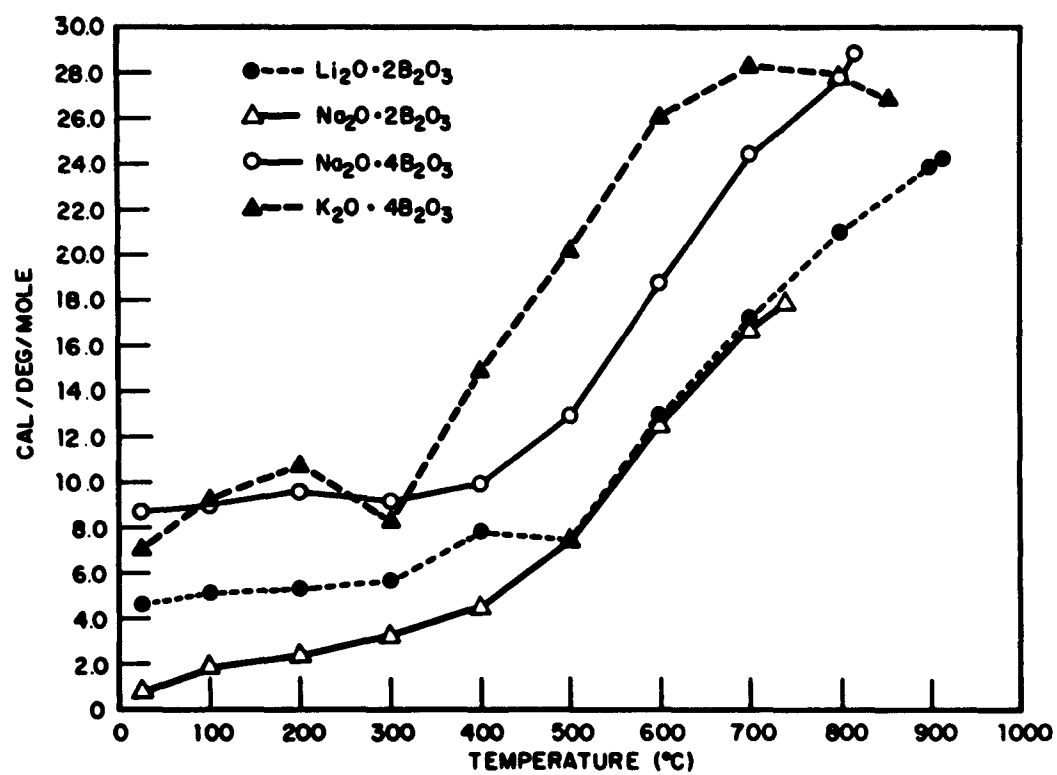


Fig. 10 Entropy of vitrification

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<p>Naval Radiological Defense Laboratory USNRDL-TR-566 VAPOR PRESSURES IN THE LIQUID SYSTEM Rb₂O-B₂O₃. DERIVED THERMODYNAMIC DATA AND A STRUCTURAL INTERPRETATION by C.E. Adams and J.T. Quan 6 June 1962 68 p. tables illus. 39 refs. UNCLASSIFIED</p> <p>By use of the transpiration method, the vapor pressures of the liquid system Rb₂O-B₂O₃ between pure B₂O₃ and Rb₂O · B₂O₃ have been measured. The vapor over the entire composition range was an equi-molar mixture of Rb₂O and B₂O₃. Data from (over)</p>	<p>1. Rubidium oxide - Chemical reactions. 2. Boron oxide - Chemical reactions. 3. High temperature research. 4. Vapor pressure - Measurement. I. Adams, C.E. II. Quan, J.T. III. Title.</p> <p>UNCLASSIFIED</p>
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